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Anomalous restoration of graphitic layers from graphene oxide in ethanol environment at ultrahigh temperature using solar furnace

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The restoration of graphitic structures from defective graphene oxide was examined in a reactive ethanol environment at ultrahigh temperatures. Structural analysis by Raman spectroscopy indicates that turbostratic structures as well as high crystallinity in multilayer graphene were accomplished by an ultrahigh-temperature process in an ethanol environment. This phenomenon is quite anomalous since it is in striking contrast to the results observed in inert environments, where graphitization proceeds significantly to form a Bernal stacking multilayer graphene. The suppression of graphitization in ethanol environments is probably caused by the simultaneous supply of carbon and etching species during the restoration process. © 2016 The Japan Society of Applied Physics

Graphene, which is a two-dimensional carbon sheet, is a promising material for various innovative applications because of such unique physical properties as high carrier mobility and extraordinary thermal/mechanical properties.^{1–5)} To meet practical demands for the applications, the large-scale production of highly crystalline graphene is a crucial issue. Graphene oxide (GO) has attracted considerable attention because of its mass-production features due to chemical exfoliation from bulk graphite using a solution process.^{6,7)} However, considerable defects, such as the adduct of oxygen-containing groups and lattice vacancies, are formed during the synthesis process and degrade the superior properties of graphene. Therefore, crystalline graphene structures must be restored by reducing the oxidized area and healing the defects.⁸⁾ Various methods have been reported for structural restoration such as a chemical process using hydrazine⁹⁾ and high-temperature heating under conditions of vacuum or inert gas^{10,11)} and under reactive environments including carbon-containing gases such as hydrocarbons and ethanol.^{12–14)} The high-temperature process in ethanol vapor is especially effective for restoring graphene structures from GO.^{13,14)} However, even if GO is heated in an ethanol environment at 1100 °C, which is the maximum temperature of a typical chemical vapor deposition (CVD) apparatus, the crystallinity of the obtained GO is less sufficient for device applications than CVD graphene grown on a metal catalyst.¹⁵⁾ Therefore, processes at much higher temperatures must be explored to improve the crystallinity of the processed GO.

Recently, several works have been reported where the ultrahigh-temperature treatments of GO at around 2000 °C or above markedly improved the crystallinity.^{16–18)} In these works, however, the process conditions were restricted to vacuum or inert environments. In addition, graphitization, namely, the formation of ordered Bernal stacking structures, proceeds in randomly oriented GO aggregates by ultrahigh-temperature treatments in inert atmospheres. Graphitization is not desirable for applications of the processed GO to electronic devices because few-layer graphene with Bernal stacking, as well as three-dimensional bulk graphite, shows a semimetallic property, which is completely different from single-layer graphene.¹⁹⁾ In the last decade, it was theoretically predicted that multilayer graphene with turbostratic stacking structures behaves as arrays of single-layer graphene

or a zero-gap semiconductor with linear dispersion around the K point;²⁰⁾ this prediction was experimentally confirmed using angle-resolved photoemission spectroscopy.²¹⁾ This feature appears quite suitable for electronic applications of graphene since such a quasi single-layer behavior makes it possible to manage both switching by a field effect and large current capacity. To achieve the best performance of the turbostratic multilayer graphene, the in-plane crystallinity of each graphene layer must be extensively improved by healing the defects in the pristine GO without extending the out-of-plane periodicity. The previously reported processes in inert environments, however, failed to maintain turbostratic structures after heating at ultrahigh temperatures,^{16,17)} and a new process is anticipated for solving this issue by achieving both high in-plane crystallinity and turbostratic structures.

In this paper, we report the formation of highly crystalline multilayer graphene with turbostratic stacking by an ultrahigh-temperature process under an ethanol environment using a solar furnace. Solar furnaces are very handy and simple to operate, and can easily be applied to reactive environments since they only heat samples at specific positions at around 2000 °C.²²⁾ We applied a solar furnace to heat GO under an ethanol environment at a reduced pressure for the first time and compared the effect of the ethanol environment in ultrahigh-temperature annealing on the stacking structure of GO with that of an inert environment.

A schematic drawing of our experimental system is shown in Fig. S1 (see the online supplementary data at <http://stacks.iop.org/APEX/9/025103/mmedia>). This system is composed of a solar furnace, a reaction chamber, and gas supply and evacuation facilities. The solar furnace consists of a Fresnel lens ($1 \times 1.4 \text{ m}^2$) and a manual sun-tracking system. Graphite was used as the material for crucibles and substrates. Sapphire and zirconia, both of which are known as high-melting-point materials, could not be used as substrates because of carbothermal reaction²³⁾ between these materials and carbon under an ultrahigh-temperature process at around 1800 °C. Commercially available dry GO flakes composed of aggregated single-layer GO (Graphene Laboratories) were dispersed on the substrates. Then, the GO flakes were treated at an ultrahigh temperature (1200–2000 °C) by irradiating the concentrated sunlight that was focused on the sample area ($1 \times 1 \text{ cm}^2$) under an inert or reactive environment. In the

case of the inert environment, we used nitrogen (N_2) gas (99.999%) at an atmospheric pressure and a reduced pressure (430 Pa). N_2 gas caused a virtually identical behavior for GO restoration to argon (Ar) gas, which is commonly used as an inert environment gas (see Fig. S2 in the online supplementary data at <http://stacks.iop.org/APEX/9/025103/mmedia>). In a reactive environment, ethanol was supplied as a reactive agent in addition to N_2 as the carrier gas. The total pressure of the mixture gas was regulated to 480 Pa. The temperature of the sample was monitored using an optical pyrometer with a Si photodetector (emissivity of 0.8 was assumed for the graphene and graphite samples) and verified by observing the melting points of various metals.

The structural restoration of GO was analyzed by Raman spectroscopy with 532 nm laser excitation. A D band originating from the disordered graphitic structures and its overtone (2D band) were clearly observed in the Raman spectra from the processed GO at around 1350 and 2700 cm^{-1} , respectively.²⁴⁾ The relative intensity ratios of the D and 2D bands to the G band in the Raman spectra [denoted as $I(\text{D})/I(\text{G})$ and $I(2\text{D})/I(\text{G})$] were evaluated as helpful guidelines for GO restoration because $I(\text{D})/I(\text{G})$ corresponds to the distance between defects.²⁵⁾ The intensity and signal shape of the 2D band are also very sensitive to the stacking structure and the number of layers of multilayer graphene.^{26–28)} In this study, the stacking orders of the graphene membranes obtained from the stacked GO were analyzed on the basis of $I(2\text{D})/I(\text{G})$ and the spectral width of their 2D bands.

Figure 1 shows the Raman spectra obtained from the GO samples under various conditions. The GO samples after the thermal processes produce distinct 2D bands in their Raman spectra [Figs. 1(a)–1(e)], while no 2D band is observed from the pristine GO. This result indicates that thermal treatments at high temperatures are very effective for the restoration of graphene structures from the defective GO, as previously reported.¹⁶⁾ The solar furnace system is a practical tool for graphene restoration from GO since it can easily generate an ultrahigh temperature of more than 1200 °C even under reactive environments. The crystallinity of the processed GO can be analyzed qualitatively from $I(\text{D})/I(\text{G})$ and $I(2\text{D})/I(\text{G})$ in the Raman spectra. As the process temperature increases to 1800 °C, $I(\text{D})/I(\text{G})$ markedly decreases and $I(2\text{D})/I(\text{G})$ markedly increases. Thermal treatments in an ethanol environment up to 1000 °C efficiently restored graphene structures from GO.¹³⁾ Our result indicates that the process in ethanol continues to be effective for improving the crystallinity of the processed GO beyond the previously reported temperature (1000 °C) and its effect is greatly enhanced for higher temperatures. The GO processed in ethanol at 1800 °C exhibits excellent features of D and 2D bands in a Raman spectrum, and its crystallinity is comparable to that of CVD-grown graphene.¹⁵⁾ In this marked restoration process, the ethanol environment plays an important role in addition to the ultrahigh temperature. Similar $I(\text{D})/I(\text{G})$ ratios are observed in Figs. 1(b) and 1(d), indicating that a comparable crystallinity was achieved under an ethanol environment at a much lower temperature. A comparison of Figs. 1(a) and 1(d) indicates that the processes at almost the same temperature cause much lower $I(\text{D})/I(\text{G})$ ratios for an ethanol environment than for a N_2 environment. In the defect healing process, it should be noted that carbon species decomposed

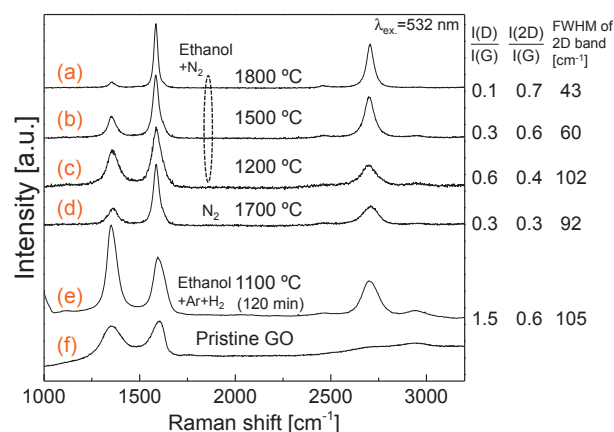


Fig. 1. Raman spectra observed from GOs processed under various conditions and $I(\text{D})/I(\text{G})$, $I(2\text{D})/I(\text{G})$, and FWHM of 2D band for evaluation of crystallinity and stacking structure. (a)–(c) Processed for 10 min in ethanol environment using solar furnace. Process temperatures are indicated. (d) Processed for 10 min in N_2 environment at 1700 °C using solar furnace. (e) Processed for 120 min in ethanol environment at 1100 °C using conventional CVD apparatus. (f) Pristine GO without any thermal process for comparison. Raman spectra were taken with 532 nm laser excitation.

from ethanol may be provided to defect sites, resulting in a detectable weight increase of GO. The undesired deposition of an additional carbon layer should be negligible for the process conditions in this study.¹⁴⁾ Accordingly, the density of defects healed in ethanol may be estimated by comparing the weight changes of GO samples processed in ethanol and N_2 . In our experiments, however, it is very difficult to measure the weight of the processed GO precisely, since our experiments are performed outdoors and part of the processed GO may be blown away during unloading the sample from the reaction chamber. Further experimental improvements are required for precise measurements of the weight change.

As mentioned above, several authors reported that the ultrahigh-temperature process in inert environments effectively restores graphene from GO.^{16–18)} Rozada et al. repaired GO defects by a process including reduction by hydrazine and subsequent two-step heating in Ar at 1500 °C and at a higher temperature (1800–2700 °C), resulting in the formation of highly crystalline graphene [$I(\text{D})/I(\text{G}) \sim 0.1$].¹⁷⁾ Ghosh et al. also reported the significant restoration of graphene from GO by a combination of chemical reduction using hydrazine and ultrahigh-temperature heating in a vacuum at 1900 °C.¹⁸⁾ In both studies, the stacking order between the restored graphene layers formed graphitized structures such as bulk graphite. The signal shape and intensity of the 2D band are closely related to the interlayer interactions in multilayer graphene.²⁸⁾ Consequently, the states of the stacking order in the processed GO can be revealed by analyzing the signal shape of 2D bands. As shown by the 2D bands in Figs. 1(b) and 1(d), their signal shape critically depends on the process environment as evaluated by FWHM, even though essentially similar D band intensities were observed. This fact strongly suggests that the stacking structure can be varied by the process environment.

Figure 2 shows typical results of the detailed analysis of the 2D bands observed after various heating processes. According to Cançado et al.,²⁶⁾ the 2D band of the Raman spectrum from multilayer graphene can be fitted by three components of Lorentzian peaks: $G'_{3\text{DA}}$, $G'_{2\text{D}}$, and $G'_{3\text{DB}}$. The volume ratio R of the Bernal stacking 3D graphite to all

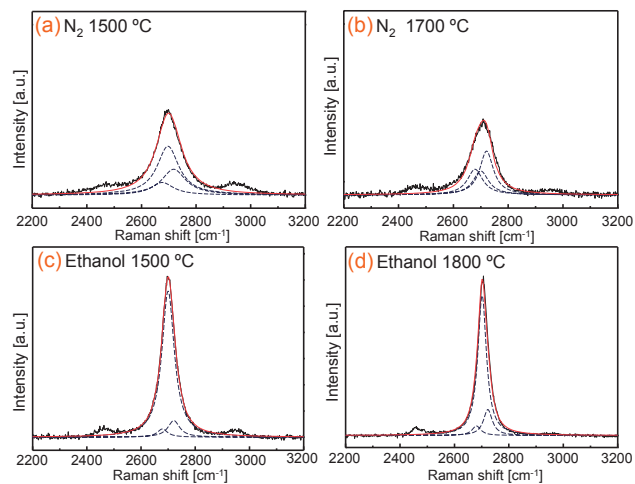


Fig. 2. Peak-fitting analysis of 2D bands observed from processed GOs: (a) Processed in N₂ at 1500 °C for 10 min. (b) Processed in N₂ at 1700 °C for 10 min. (c) Processed in ethanol environment at 1500 °C for 10 min. (d) Processed in ethanol environment at 1800 °C for 10 min.

Table I. Summary of 2D-band peak-fitting analysis.

Environment	Temperature (°C)	$I(D)/I(G)$	$I(2D)/I(G)$	R (%)
N ₂	1500	0.6	0.3	30
N ₂	1700	0.3	0.3	60
Ethanol	1500	0.3	0.6	10
Ethanol	1800	0.1	0.7	20

stacking structures, including turbostratic stacking, can be analyzed using the following formula:

$$R = \frac{I(G'_{3DB})}{I(G'_{3DB}) + I(G'_{2D})},$$

where $I(G'_{3DB})$ and $I(G'_{2D})$ denote the intensities of the G'_{3DB} and G'_{2D} signals, respectively. In peak-fitting analysis, the center positions of the G'_{3DA} , G'_{2D} , and G'_{3DB} signals were fixed to be around 2680, 2700, and 2720 cm⁻¹, respectively.^{17,26} Table I shows the analysis results. For the inert N₂ environment, the volume ratio of the 3D graphite (R) rapidly increased from 30 to 60% as the process temperature rose from 1500 to 1700 °C. This observed phenomenon is consistent with previously reported results.^{16–18} However, the situation is completely different for the reactive ethanol environment. Even after the thermal process at 1800 °C, R maintains a quite low value very similar to that for 1500 °C. This result means that turbostratic stacking structures are formed in ethanol environments by the ultrahigh-temperature process of single-layer GO aggregates with random orientations, suggesting the effect of ethanol of suppressing the graphitization of the processed graphene even at ultrahigh temperatures. The formation of a turbostratic structure at an ultrahigh temperature, which is in striking contrast to the graphene processed in N₂ environments, is a quite anomalous phenomenon.

Unfortunately, the origin of the suppressed graphitization observed for ethanol environments remains unknown, but we speculate that this phenomenon is specifically related to the difference between the microscopic mechanism in the defect-healing processes of GO under ethanol and inert gas envi-

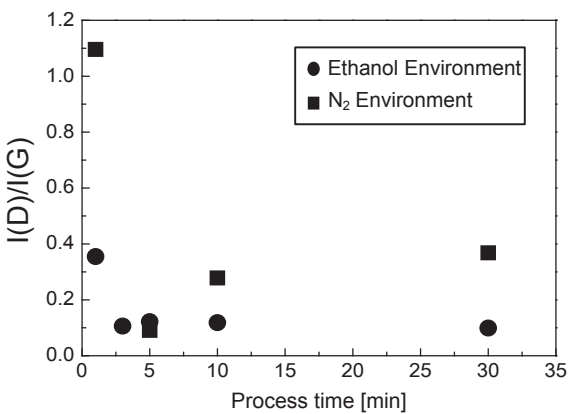


Fig. 3. Comparison of $I(D)/I(G)$ observed from GOs processed for various times at 1700 °C in inert N₂ or at 1800 °C in ethanol environments.

ronments. Actually, we observed a striking difference in the restoration behavior of GO between these environments, as shown in Fig. 3 and Fig. S3 in the online supplementary data at <http://stacks.iop.org/APEX/9/025103/mmedia>.

For the thermal process at 1700 °C in the inert environment [Fig. S3(a) in the online supplementary data at <http://stacks.iop.org/APEX/9/025103/mmedia>], the weak 2D band observed after heating for one minute became significantly intense after 5 min of heating, and its intensity was maintained after longer heating processes. Judging from the signal shape of the 2D band, graphitization already proceeded after heating for 5 min. Analysis of the 2D signal shapes indicates that the ratio of Bernal stacking R became 60% after heating for 5 min and remained constant for subsequent heating. The behavior of the D band, however, is inconsistent with that of the 2D band as shown in Fig. 3. The D band intensity reached a minimum after heating for 5 min and became larger during longer heating. This result means that the defect healing of GO to form graphene was terminated by heating for 5 min, and then additional defects were revealed. This undesired damage to the restored graphene may have been caused by attacks from such reactive species as trace amounts of impurities contained in high-purity N₂ gas (99.999%) and possibly very small leakage from the connections between gas pipes. Even though the detailed structure of the defects formed during the heating remains undetermined, it should be very stable even at ultrahigh temperature and quite different from the defects that originally formed in the pristine GO by chemical processes, which can be easily repaired at ultrahigh temperature.

In an ethanol environment, the behavior of the Raman spectra from the GO treated at 1800 °C for various heating times is distinct from that in the N₂ environment. As shown in Fig. S3(b) in the online supplementary data at <http://stacks.iop.org/APEX/9/025103/mmedia>, a clear 2D band appears even after heating for one minute. Its intensity and signal shape do not change after longer heating times, indicating repair of the defects in GO and the extension of a conjugated π -electron system without interlayer ordering into Bernal stacking. The D band intensity, observed after various heating times, also behaves in accordance with the 2D bands. As shown in Fig. 3, the $I(D)/I(G)$ ratios became weaker by heating for 3 min and fairly fine $I(D)/I(G)$ ratios were preserved after longer heating processes. This result shows

that defect repair was terminated by 3 min and no additional defects were revealed in contrast to the results in the N₂ environment. The residual impurities contained in the process environments probably form additional defects that are not repaired by heating in the N₂ environment. In the ethanol environment, consequently, the defects induced by the residual impurities must be healed, resulting in virtually constant defect density by chemical equilibrium between defect forming and healing reactions. Peak shape analysis of the 2D bands shows that the ratio of Bernal stacking R stays at very low values of around 10–20% throughout the heating process.

The supply of carbon and etching species in ethanol environments may cause a difference in defect-healing mechanisms and graphitization effects. In the N₂ environment, no carbon and etching species are supplied. Carbon atoms around defect sites should actively move around in the graphene lattice and migrate on the surface at ultrahigh temperatures and find energetically stable positions to form Bernal stacking. In ethanol environments, on the other hand, etching species containing oxygen in addition to carbon species are effectively supplied and the carbon atoms around the defect sites do not need to move actively to rearrange carbon bonding in graphene sheets to heal the defects. Accordingly, graphitization must be suppressed in ethanol environments. The mechanism for the suppression of graphitization effects proposed here is only speculative and further studies are necessary to fully understand this anomalous phenomenon.

In summary, very defective GO was processed for the first time in a reactive ethanol environment at ultrahigh temperature around 1800 °C using a solar furnace. Detailed analysis of processed GO demonstrates that multilayer graphene was formed in quite high crystallinity comparable to that of CVD-grown graphene; its stacking structure was not Bernal stacking, which is usually observed for ultrahigh temperature processes in inert environments, but a turbostratic structure. This quite anomalous phenomenon indicates that the ethanol environment effectively suppressed graphitization to transform from randomly stacked GO sheets to regularly ordered Bernal stacking graphite structures. The origin for the suppression of graphitization in ethanol environments is still unknown, but it is probably closely related to gas phase composition during the restoration process, where carbon species for healing defects and oxygen-containing species for etching unstable carbons are simultaneously supplied to GO surfaces. Further analysis using X-ray diffractometry, transmission electron microscopy, and carrier transport measurements should be necessary to approach the actual mechanism suppressing the graphitization in forthcoming

investigations. The new process at ultrahigh temperature in reactive environments established in this study is very useful for producing turbostratic multilayer graphene with high crystallinity. This technique will be available for exploring various applications of turbostratic graphene, such as quasi single-layer electronics and functional graphene membranes with high thermal/electrical conductivities in future studies.

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